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Designation: Process for manufacturing small-particled polyolefin molded materials containing fibrous additives and their use in manufacturing molded bodies

Applicant: BASF AG, 6700 Ludwigshafen

Inventor: Theysohn, Rainer, Dipl.-Chem, Dr., 6700 Ludwigshafen
Zeitler, Gerhard, Dipl.-Chem., Dr., 6711 Hessheim
Pfirmann, Günther, Dipl.-Chem, Dr.,
Seiler, Erhard, Dipl. Chem, Dr., 6700 Ludwigshafen

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Patent Claims

1. Process of manufacturing small-particled, polyolefin molded masses containing fibrous additives, which are formed from
 - a) 100 parts by weight of a small-particled, semi-crystalline polyolefin, which has an average particle diameter within a range of 10 μm to 5000 μm and exhibits an intrinsic viscosity $[\eta]$ within a range of 0.5 to 15, measured in "Decalin" at 130°C;
 - b) 2 to 150 parts by weight of a fibrous additive, which has an average particle diameter of 0.0001 μm to 200 μm , an average fiber length of 1 to 5000 μm , and a softening temperature of at least 50°C above the crystallite melting temperature of polyolefin, as well as
 - c) 0 to 5 parts by weight of a standard bonding agent with a silane or titanate base, as well as
 - d) normal amounts of other standard additives or reagents, as the case may be,

thereby distinguished by the fact that one mixes the components (a) and (b) as well as (c) and/or (d), as the case may be,

in a mixer during the first work cycle (I) subject to application or removal of caloric heat, as the case may be, whereby

during the first subcycle (I.1) with a mixing force within a 100 to 600 W/l useful content range within a time interval of 2 to 30 minutes [one] brings [the components] to the crystallite melting temperature of polyolefin (a) from an

ambient temperature, specifically room temperature, below the crystallite melting temperature of polyolefin (a); immediately thereafter

during a second subcycle (I.2) [one] switches to a mixing force that is 0.3 to 0.8 times greater than the mixing force of the first subcycle (I.1), and within a time interval of 0.1 to 20 minutes brings [the mixture] from the crystallite melting temperature of polyolefin (a) to a temperature 3° to 40° above the crystallite melting temperature; immediately thereafter,

during a second work cycle (II) discharges the mixture from the mixer within a time interval of 0.5 to 30 seconds and brings the mixture to a temperature below the crystallite melting temperature of polyolefin (a) within 120 seconds.

2. Use of small-particled, polyolefin molding materials containing fibrous additives [defined] according to Claim 1 for manufacturing molded bodies by means of standard injection molding, extrusion molding and hollow body blow molding processes.

Process of manufacturing small-particled, polyolefin molded masses containing fibrous additives and their use for manufacturing molded bodies.

This invention concerns a process for manufacturing small-particled, polyolefin molding materials, containing fibrous additives. These molding materials are formed from a) 100 parts by weight of a small-particled, semi-crystalline polyolefin which has an average particle diameter with a range of 10 μm , and 5000 μm and exhibits an intrinsic viscosity $[\eta]$ within a range of 0.5 to 15, measured in Decalin at 130°C ; b) 2 to 150 parts by weight of a fibrous additive, which has an average particle diameter of 0.001 to 200 μm , an average fiber length of 1 μm to 5000 μm and a softening temperature at least 50°C above the crystallite melting point of polyolefin; c) 0 to 5 parts by weight of a standard bonding agent with a silane or titanate base, as well as d) normal amounts of other standard additives or reagents, as the case may be.

Such non-molded polyolefin molding materials, which are filled with fibrous additives, are materials which can be manufactured by standard processes, such as, for example, injection molding or extrusion [to form] polyolefin-molded bodies filled with the additive.

The loading of polyolefin molding materials with fibrous additives, such as inorganic fillers with a fibrous structure, is a proven process for achieving satisfactory product properties, such as higher tensile strength and higher bending

strength, better dimensional stability, lower coefficient of thermal expansion or higher stiffness.

In practice, the introduction of suitable fibrous additives into polyolefins occurs in such a way that the polymer is first melted in the extruders and the fibrous filler is metered into the melt. The disadvantages of this process are first of all the high expenditure of energy necessary for melting the polyolefin and [the difficulty associated with metering] the additive into the melt; secondly, the considerable technical expenditure that must be maintained with respect to the fibrous fillers, which often tend toward blocking and bridging during precise metering and continuous feed. In addition, inorganic fibrous fillers in particular [cause] substantial wear in the area of the feed zones of the processing machines. This process is not suitable for mineral, basalt, or slag-based fibrous additives, which are interesting for cost reasons, because such [additives] — [used] mostly for insulation purposes [in] commercial products — are available only in non-meterable forms such as batting or as batting-like material. Furthermore, the aforementioned standard loading process is not suitable for such polyolefins as those that are irreversibly damaged because of their high molecular weight or because of partial crosslinking as a result of the unavoidable high specific gravity values that occur during loading.

Therefore, the problem was to develop a cost effective and exact process using simple apparatus for loading fibrous additives into small-particled polyolefin molding materials, and that avoids the disadvantages of the state of the art and leads to small-particled loaded molding materials that can be easily manufactured into homogeneous molded bodies of high quality.

The problem was resolved according to the invention by virtue of the fact that one mixes the components (a) - small-particled, semi-crystalline polyolefin, (b) - fibrous additive and, as the case may be, (c) - bonding agent, as well as (d) - other additives and reagents in a mixer in an initial work cycle (I), while subjected to application or removal of caloric heat, as the case may be; whereby during an initial subcycle (I.1), with a mixing force of 100 to 600 W/l useful content within a time interval of 2 to 30 minutes at ambient temperature, which lies below the crystallite melting temperature of polyolefin (a) and, specifically is room temperature, [one] brings [the mixture] to the crystallite melting temperature of polyolefin; immediately thereafter, during a second subcycle (I.2,) [one] switches to a mixing force that is 0.3 to 0.8 times greater than the mixing force of the first subcycle (I.1), and brings [the mixture] from the crystallite melting temperature of polyolefin (a) to a temperature 3°C to 40° above the existing temperature within a time interval of 0.1 to 20 minutes; immediately thereafter, during a second work cycle (II) [one] discharges [the mixture] from the mixer within a time interval of 0.5 to 30 seconds and brings [the mixture] to a temperature below the crystallite melting temperature of polyolefin (a) within 120 seconds.

Small-particled crystalline polyolefins (a) are those which are understood to have a particle diameter within a range of 10 μm to 5000 μm , preferably 100 μm to 2000 μm and which exhibit an intrinsic viscosity $[\eta]$ of 0.5 to 15, preferably 1 to 10 (measured in Decalin at 130°C according to DIN 53 728). Polyolefins include preferably high density polyethylene (0.93 to 0.97 g/cm³) and polypropylenes, especially such as are manufactured according to the process described in DE-AS 1 217 071 in which the copolymers of ethylene and polypropylene still retain crystalline components; as well as corresponding polymers that contain up to 5 wt. % grafted acrylic acid. Semi-crystalline polyolefins are those in which a high

melting peak occurs during DSC analysis.

~~Fibrous additives (b) shall exhibit an average particle diameter of 0.001 μm to 200 μm , preferably 0.01 to 50 μm , and the fiber length shall be 1 to 5000 μm , preferably 5 to 2000 μm .~~ (a). In addition, they shall possess a melting or softening range at least 50°C above the crystallite melting point of polyolefin. Suitable fibrous additives are glass fibers from A-, E- or C-glass, mineral fibers, cinder wool, asbestos fibers, carbon fibers, K-titanate fibers, ~~wood fibers, cellulose fibers,~~ polyamide, polyester or aramide fibers.

Suitable bonding agents are (c) standard silane or titanate compounds, such as are those sold e.g. by the Union Carbide Corp. or Kenrich Petrochemicals Inc.

Suitable additives and reagents (d) include the following: inorganic and organic paint pigments, stabilizers, processing agents, lubricating agent and mold-release agents, compatibility agents and blowing agents.

The manufacture of molding materials can occur in a mixer in which the mixing vanes are positioned perpendicular to the mixer axis as described, for example, in DE-AS 1 054 073 or DE-AS 1 454 368. Up to now such mixers were used mainly to prepare non-crystalline thermoplastics with a wide softening range, such as PVC or ABS. They are also suitable for agglomerating fine-particled polyolefins with poor free-flowing properties [and] having a wide particle distribution, so that a narrower coarse grain spectrum and a higher bulk density results, so that in this way processing performance can be improved. Moreover, it is known that the agglomeration of plastic particles can also occur in the presence of additives. The description of DE-OS 2 302 370 implies that during the preparation of polyolefin

powder in high-speed mixers, the maximum temperature should be 2°C to 13°C below the melting range of polyolefin in order to avoid sticking and/or lumping.

An unexpected result of the process described by the invention is that it is also possible to work within a temperature range above the crystallite melting point of the polymer in question without the occurrence of any appreciable agglomeration or even lumping, so that it is possible to completely bond fibrous additives (b) onto polyolefin components. The results are fine-particled molding materials that exhibit a particle distribution similar to the polymer that was used [and] that contain bonded additives (b) and can be easily processed further into molded bodies.

Another unexpected result of the process described by the invention is that it is possible to crush continuous filaments based on mineral wool and slag wool that are virtually unusable for thermoplastic processing — due to manipulation and metering in the manufacture of thermoplastics — [and] to homogeneously distribute the particles and to bond them to the polymer.

The process described in the invention is thereby distinguished by the the fact that during the initial subcycle (I.1) one brings the mixture, which is comprised of (a) and (b) and, as the case may be, (c) and/or (d) to the crystallite melting temperature of polyolefin with a mixing force of 100 to 600, preferably 200 to 400 W/l useful content within 2 to 50 [minutes], preferably 5 to 20 minutes at ambient temperature, specifically, room temperature, then subsequently during the course of a second subcycle (I.2) changes to a mixing force that increases to 0.3 to 0.8 times, preferably 0.4 to 0.7 times, greater than the mixing force of the first subcycle (I.1), and brings the mixture from the crystallite melting temperature of polyolefin to 3° to 40°, preferably 5° to 30°, above that temperature within a

time interval of 0.1 to 20. minutes, preferably 0.2 to 10 minutes.

Subsequently, the product is discharged from the mixer in a second work cycle (II) within 0.5 to 30 [seconds], preferably 0.5 to 10 seconds, and is cooled to a temperature below the polymer melting point.

The possibility also exists, however, to process the product further in its plastic state using appropriate equipment [and] without further cooling.

A variation of the mixing process consists of introducing additional fine-particled fillers, such as calcium kaoline, with an average particle size of $0.5\ \mu\text{m}$, or talc, with an average flake thickness of $1\ \mu\text{m}$, to the mixture during the course of the second subcycle (I.2); whereby the quantity of fine-particled fillers shall not exceed 30 wt. % of the fibrous additives used.

Mixing force of 100 to 600 W/l useful content is understood to mean the energy input (in watts) per liter volume occupied by the components (a), (b) and, as the case may be, (c) and/ or (d) in the mixer.

The process described is far less expensive with respect to apparatus and energy consumption than extruder fabrication. In addition, the process permits simple and exact loading of components, additives and loading materials without complicated metering techniques. Moreover, the process has the following advantage: it is possible to load fillers into otherwise difficult-to-manufacture thermoplastics, such as ultra-high molecular polyethylene, without harming the polymer. An additional

advantage is the problem-free use of cost-effective insulation glass fibers in the form of endless mats or in batting-like form.

Small-particled, polyolefin molding materials containing fibrous additives can be used for the manufacture of molded bodies by means standard injection molding, extrusion, or hollow body blow molding processes.

The following examples clarify the aforementioned process:

Example 1

The feedstock is a mixture of (a) 25 kg (corresponding to 100 parts by weight,) of a small-particled polyethylene that has a particle diameter within a range of 250 μm to 2000 μm and an average particle diameter of 800 μm , and that exhibits an intrinsic viscosity $[\eta]$ of 4.8; and (b) 4.41 kg (corresponding to 17.6 parts by weight) of cut-glass fibers [cut] from E glass [and] finished with a bonding agent and a glass fiber smoother, and that have a particle diameter of 14 μm and an average length of 6 mm in as-delivered condition. During the first work cycle (I.), the aforementioned mixture is brought to the crystallite melting temperature of polyethylene (a) ($\approx 138^\circ\text{C}$) in a fluid mixer with 100 l useful content — without application or removal of caloric heat — during the course of the initial subcycle (I.1) with a mixing force of 350 W/l useful content within a time interval of 5 minutes at ambient temperature (\approx room temperature); immediately thereafter, during a second subcycle (I.2), with a mixing force on the average 0.52 times greater than the mixing force of the first subcycle (I.1), within a time interval of 3 minutes of the crystallite melting temperature of polyethylene (a), [the mixture] is brought to a [temperature] 12°C above the existing temperature ($\approx 150^\circ\text{C}$), and immediately thereafter, the mixture is discharged from the mixer

during the course of a second work cycle (II) within a time interval of 5 seconds and is brought to a temperature ($= 75^{\circ}\text{C}$) below the crystallite melting temperature of polyethylene (a) within 30 seconds.

The fine-particled product obtained exhibits virtually the same particle distribution as the original polymer powder; the average glass fiber length is 0.21, whereby 90-95 wt. % of the glass fibers used are permanently bonded to the polymer.

Example 2

The feedstock material is a mixture comprised of (a) 20 kg (corresponding to 100 parts by weight) of a small-particled polypropylene which has a particle diameter of $25\text{ }\mu\text{m}$ to $1000\text{ }\mu\text{m}$ and an average particle diameter of $400\text{ }\mu\text{m}$ and which exhibits an intrinsic viscosity $[\eta]$ of 2.7; and (b) 5.0 kg (corresponding to 25 parts by weight) mineral fibers in the form of rock wool mat cut in strips whereby the continuous filaments have a diameter between $10\text{ }\mu\text{m}$ and $25\text{ }\mu\text{m}$; and (c) 0.05 kg (corresponding to 0.25 parts by weight) γ -aminopropyltriethoxy-silane (d) 0.1 kg (corresponding to 0.5 parts by weight) of the stabilizer Irganox PS 802 (manufactured by Ciba-Geigy, Basel).

During an initial work cycle (I.), the aforementioned mixture, in a fluid mixer of 100 l useful content — without application or removal of caloric heat — is brought to the crystallite melting temperature of polypropylene (a) ($= \approx 160^{\circ}\text{C}$) during the course of an initial subcycle (I.1) with a mixing force of, on the average, 320 W/l useful content within a time interval of 4.6 minutes at ambient temperature ($=$ room temperature); immediately thereafter, during the course of a second subcycle (I.2), the mixture, with a mixing force on the average 0.47 times greater than the mixing force of the first subcycle (I.1) within a time interval of 3.2 minutes is

brought from the crystallite melting temperature of polypropylene to a [temperature] 10°C above the existing temperature ($= 170^{\circ}\text{C}$); and immediately thereafter, during a second work cycle (II), the mixture is discharged from the fluid mixer within a time interval of 5 seconds and is brought within 50 seconds to a temperature (80°) below the crystallite melting point of polypropylene (a).

The product contains the completely disintegrated mineral fibers, which have been reduced to an average length of 0.17 mm and which are 98% completely bonded with respect to the fiber quantity introduced.

Example 3

The feedstock is a mixture comprised of (a) 20 kg (corresponding to 100 parts by weight) of a small-particled, acrylic acid-grafted polypropylene which has an acid count of 30, (see DE-OS 26 58 810), which has a particle diameter within a range of $50\text{ }\mu\text{m}$ to $1500\text{ }\mu\text{m}$ and an average particle diameter of $500\text{ }\mu\text{m}$ and which exhibits an intrinsic viscosity $[\eta]$ of 4 ($\text{MI} = 0.1, 2.16\text{ kg. }230^{\circ}\text{C}$); and (b) 5.0 kg (corresponding to 25 parts by weight) of cut-glass fibers cut from E-glass, which are finished with a bonding agent and a glass fiber smoother, [and] which have a maximum fiber diameter of $14\text{ }\mu\text{m}$ and, in the initial state, an average length of 3 mm. During an initial work cycle (I), the aforementioned mixture, in a fluid mixer of 100 l useful content — without application or removal of caloric heat — is brought to the crystallite melting of the grafted polypropylene (a) ($= \approx 160^{\circ}\text{C}$) during an initial subcycle (I.1) with a mixing force of 345 W/l useful content within a time interval of 5.2 minutes at ambient temperature ($=$ room temperature); immediately thereafter, during the course of a second subcycle (I.2) with a mixing force which, on the average, is 0.50 times the mixing force of the first subcycle (I.1), the mixture is brought from the crystallite melting temperature of the

modified polypropylene to a [temperature] 14°C above the existing temperature ($= 174^{\circ}\text{C}$) within a time interval of 5 minutes; immediately thereafter, during a second work cycle (II.), the mixture is discharged from the fluid mixer within a time interval of 5 seconds and is brought within 50 seconds to a temperature ($= 80^{\circ}\text{C}$) below the crystallite melting point of polypropylene (a).

The fine-particled product has a particle size distribution which is somewhat finer than that of the initial polymer product. The fibers, which are virtually completely bonded, have an average length of 0.15 mm.

Example 4

The feedstock is a mixture comprised of (a) 16 kg (corresponding to 100 parts by weight) of a small-particled polypropylene which has a particle diameter within a range of $25\text{ }\mu\text{m}$ to $1000\text{ }\mu\text{m}$ and an average particle diameter of $400\text{ }\mu\text{m}$ and which exhibits an intrinsic viscosity $[\eta]$ of 2.7; and (b) 4 kg (corresponding to 25 parts by weight) [of] wood fibers from spruce/fir-wood with a fiber length between $30\text{ }\mu\text{m}$ and $200\text{ }\mu\text{m}$ and a fiber thickness within a range of $1\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$, whereby the average l/d ratio is 8 : 1. During an initial work cycle (I.), the aforementioned mixture, in a fluid mixer of 100 l useful content — without application or removal of caloric heat — is brought to the crystallite melting temperature of polypropylene (a) ($= 160^{\circ}\text{C}$) during the first subcycle (I.1) with a mixing force of 200 W/l useful content within a time interval of 7.5 minutes at ambient temperature ($=$ room temperature); immediately thereafter, during the course of a second subcycle (I.2), with a mixing force which, on the average, is 0.52 times greater than the mixing force of the first subcycle (I.1), the mixture is brought from the crystallite melting temperature of the polypropylene (a) to a temperature 14°C above the existing temperature ($= 174^{\circ}\text{C}$) within a time

interval of 1.5 minutes; immediately thereafter, during a second work cycle (II.), the mixture is discharged from the fluid mixer within a time interval of 5 seconds and brought within 45 seconds to a temperature ($= 75^{\circ}\text{C}$) below the crystallite melting point of polypropylene.

The fine-particled product is free-flowing, contains 90 % of the introduced filler, which is firmly bonded and is virtually odor-free.